Organometallics **1992,** *11,* 350–356

Organolanthanide-Induced C–C Bond Formation. Preparation and Properties of Monomeric Lanthanide Aldolates and Enolates

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Received May 7, 1991

The reactivity of early-lanthanide carbyls $Cp^*_2LnCH(SiMe_3)_2$ (**1**, Ln = La; **2**, Ln = Ce) toward ketones has been studied. No reaction was observed with the bulky di-*tert*-butyl ketone. The corresponding lanthanum hydride $[Cp^*_2LaH]_2$ (**3**) is more reactive and afforded the addition product $Cp^*_2LaOCH(t\text{-}Bu)_2{\cdot}O{=}C(t\text{-}Bu)_2$ (**4**). Hydrogen transfer and formation of lanthanide aldolates $Cp^*_2LnOCMe_2CH_2C({=}O)Me$ (**5**, Ln = Ce; **6**, Ln = La) together with the protonated carbyl $CH_2(SiMe_3)_2$ were observed when **1** or **2** was treated with acetone. The molecular structure of the cerium analogue **5** was determined by X-ray diffraction and was found to be a monomeric bent metallocene compound with a η^2-coordinated aldol fragment. Cell data: monoclinic, $P2_1/n$, $a = 10.386$ (5) Å, $b = 17.32$ (1) Å, $c = 14.488$ (3) Å, $\beta = 99.33$ (3)°, D_{calcd} (Z = 4) = 1.36 g·cm^{-3}. Least-squares refinement based on 3343 reflections converged to $R = 0.035$ and $R_w = 0.041$. Addition of 3-pentanone to the carbyls **1** and **2** did not result in C–C coupling but provided enolate–ketone adducts $Cp^*_2LnOC(Et){=}C(H)Me{\cdot}O{=}CEt_2$ (**7**, Ln = La; **8**, Ln = Ce). Reactions of the carbyls **1** and **2** with 4-methyl-5-hydroxy-5-ethyl-3-heptanone yielded the enolate–ketone adducts as well and suggest that the differences in reactivity between acetone and 3-pentanone are thermodynamic and not kinetic in origin.

Introduction[1]

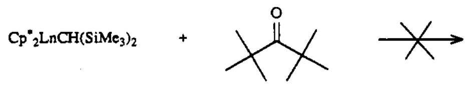
Currently, there is considerable interest in the use of organolanthanides in organic synthesis.[2] One such topic is the formation of C–C bonds by the addition of carbonyl compounds to organolanthanide species containing Ln–C or Ln–H σ bonds.[3] Imamoto and co-workers[3a] have recently shown that organocerium alkyls, prepared in situ from cerium(III) iodides and alkyllithium reagents, react with ketones at low temperature to give the corresponding tertiary alcohols in excellent yield. The 1,2-addition products were predominantly formed, even with enolizable ketones such as acetophenone. π-Allyllanthanide compounds $Ln(\pi\text{-allyl})_4Li$ (Ln = Ce, Nd, Sm) display similar reactivity and have been shown to be highly 1,2-regioselective allyl-transfer reagents for α,β-unsaturated carbonyl compounds.[3b] The yields and selectivity of the reactions are much higher than for main-group reagents such as allyllithium. The strong oxophilicity of lanthanide metals, in combination with their hardness, is assumed to be responsible for these high regioselectivities.

Carbonyl chemistry is not limited to alkyl/allyl transfer reactions only. For instance, cerium enolates, prepared from lithium enolates and $CeCl_3$, undergo aldol reactions with ketones or sterically hindered aldehydes to afford the corresponding β-hydroxy ketones in high yields.[4a] Kagan et al. have reported[4b] that the reaction of SmI_2 with a large excess of butanone followed by acid workup resulted in the almost exclusive formation of 5-methyl-5-hydroxy-3-heptanone, one of the possible butanone ketols. Recently, Streitwieser and co-workers[4c] demonstrated that $[Cp''_2YbCl]_n$ is an efficient catalyst for the reaction of silyl ester enolates with aliphatic and aromatic aldehydes to yield β-siloxy esters with useful diastereoselectivity.

Despite the interest in this area, studies aimed at identifying the organolanthanide species involved in the reaction sequence, possibilities of which include lanthanide–ketone adducts, alkoxides, enolates, and aldolates, are scarce. Furthermore, factors that determine the regioselectivity of the reactions, i.e. 1,2-addition, 1,4-addition, or enolization, are not well understood. With well-defined monomeric lanthanide carbyls $Cp^*_2LnCH(SiMe_3)_2$ (Ln = La, Ce) available,[5] we decided to investigate their reactivity toward simple ketones such as acetone, 3-pentanone, and di-*tert*-butyl ketone in more detail. In this article we demonstrate that the outcome of these reactions depends strongly on the ketone employed.

Results and Discussion

The carbyls $Cp^*_2LnCH(SiMe_3)_2$ (**1**, Ln = La; **2**, Ln = Ce) failed to react with di-*tert*-butylketone (NMR tube reaction, eq 1). Even after several days at 50 °C, characteristic



(1)

resonances of the starting materials were still present.

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(1) The following abbreviations are used in this article: Ln = lanthanide or group 3 element; Cp* = η^5-C_5Me_5; Cp″ = η^5-bis(1,3-trimethylsilyl)cyclopentadienyl; lw = line widths of the NMR resonances at half-maximum.

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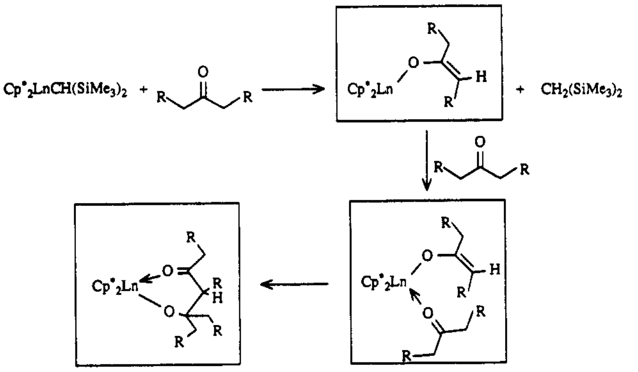
Table I. NMR Data (δ) for Compounds 4–8[a]

$Cp^*_2LaOCH(t\text{-}Bu)_2\cdot O{=}C(t\text{-}Bu)_2$[b] (4)	3.74, 1.96, 1.09, 1.04	(s, 1 H, CH), (s, 30 H, Cp*), (s, 18 H, *t*-Bu), (s, 18 H, *t*-Bu)
	120.0, 91.7, 38.6, 30.1, 28.9, 11.3	(s, C_5Me_5), (d, $^1J_{CH}$ = 135 Hz, OCH), (s, *t*-Bu), (q, $^1J_{CH}$ = 124 Hz, *t*-Bu), (q, $^1J_{CH}$ = 127 Hz, *t*-Bu), (q, $^1J_{CH}$ = 125 Hz, C_5Me_5)
$Cp^*_2CeOCMe_2CH_2C({=}O)Me$ (5)	21.7, 15.6, 1.09, -1.03	(s, 2H, lw = 31 Hz, CH_2), (s, 6 H, lw = 16 Hz, 2 Me), (s, 30 H, lw = 15 Hz, Cp*), (s, 3 H, lw = 8 Hz, Me)
$Cp^*_2LaOCMe_2CH_2C({=}O)Me$ (6)	2.24, 2.06, 1.72, 1.13	(s, 2 H, lw = 6 Hz, CH_2), (s, 30 H, Cp*), (s, 3 H, lw = 3 Hz, Me), (s, 6 H, lw = 6 Hz, 2 Me)
$Cp^*_2LaOCEt{=}C(H)Me\cdot O{=}CEt_2$ (7)	4.26, 2.10, 2.00, 1.87, 1.82, 1.18, 0.68	(q, 1 H, *J* = 6.6 Hz, =CH), (q, 2 H, *J* = 7.4 Hz, CH_2), (s, 30 H, Cp*), (q, 4 H, *J* = 7.3 Hz, 2 CH_2), (d, 3 H, *J* = 6.6 Hz, Me), (t, 3 H, *J* = 7.4 Hz, Me), (t, 6 H, *J* = 7.3 Hz, 2 Me)
	226.8, 161.5, 118.1, 88.2, 36.1, 32.7, 13.3, 12.8, 10.8, 8.7	(s, C=O), (s, OC=), (s, Cp*), (d, $^1J_{CH}$ = 150 Hz, =CH), (t, $^1J_{CH}$ = 126 Hz, CH_2), (t, $^1J_{CH}$ = 120 Hz, CH_2), (q, $^1J_{CH}$ = 125 Hz, Me), (q, $^1J_{CH}$ = 128 Hz, Me), (q, $^1J_{CH}$ = 125 Hz, Cp*), (q, $^1J_{CH}$ = 130 Hz, Me)
$Cp^*_2CeOCEt{=}C(H)Me\cdot O{=}CEt_2$ (8)	10.8, 8.2, 3.0, 2.8, 0.5, -6.0, -10.7	(s, 1 H, lw = 17 Hz, =CH), (s, 2 H, lw = 22 Hz, $=CCH_2$), (s, 3 H, lw = 15 Hz, Me), (s, 30 H, lw = 6 Hz, Cp*), (s, 3 H, lw = 14 Hz, Me), (s, 6 H, lw = 50 Hz, 2 Me), (s, 4 H, lw = 150 Hz, 2 CH_2)

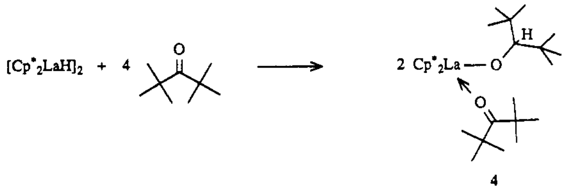
[a] All spectra were recorded in benzene-d_6 at 21 °C. [b] Assignment of the carbonyl and one of the internal *t*-Bu carbons was not possible.

Scheme I



Coordination of the carbonyl moiety to the metal center, a prerequisite for further reactivity, is likely to be inhibited by steric repulsion between the bulky $CH(SiMe_3)_2$ ligand and the ketone *tert*-butyl groups.

In order to test this, the reaction was also carried out with the corresponding lanthanum hydride $[Cp^*_2LaH]_2$ (3). This compound is known to be dimeric in solution (cryoscopy),[5b] but it is generally assumed that a coordinatively very unsaturated monomeric hydride, formed by dissociation of the dimer, is the reactive species.[6] Addition of an excess of di-*tert*-butyl ketone to 3 resulted in a rapid reaction to form the novel lanthanide alkoxide–ketone adduct $Cp^*_2LaOCH(t\text{-}Bu)_2\cdot O{=}C(t\text{-}Bu)_2$ (4) (eq 2).



(2)

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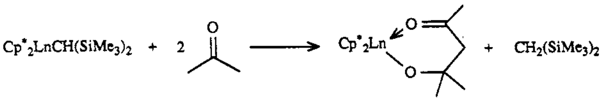
Alkoxide 4 was isolated as a yellow crystalline solid in reasonable yield. It shows characteristic downfield-shifted resonances for the OCH moiety at δ 3.74 (^1H NMR) and δ 91.7 ppm (^{13}C NMR, d, $^1J_{CH}$ = 135 Hz; Table I). The IR spectrum displays a broad absorption for the coordinated carbonyl moiety at 1630 cm^{-1}. This band is significantly shifted to lower energy compared to the carbonyl stretching vibration of free nonconjugated ketones, which is a strong indication that the carbonyl group is coordinated to the Lewis acidic cerium center.[7]

A very different result was obtained when the carbyls 1 and 2 were allowed to react with enolizable ketones such as acetone and 3-pentanone. Upon addition of 2 mmol of acetone to carbyl 2, a single organocerium compound was formed together with the quantitative liberation of $CH_2(SiMe_3)_2$ (NMR). Spectroscopic data (IR, NMR; Table I) and an X-ray diffraction study (vide infra) show that two molecules of acetone are coupled at the metal center in an aldol fashion (eq 3).



5, Ln= Ce;

6, Ln= La

(3)

The cerium aldolate 5 was isolated as hydrocarbon-soluble, deep red crystals in 53% yield. Its IR spectrum shows a strong, low-field-shifted carbonyl absorption at 1660 cm^{-1}. Trivalent cerium is paramagnetic ($4f^1$), and consequently the ^1H NMR resonances are isotropically shifted and broadened. An ^1H NMR spectrum of 5 is in accordance with the proposed structure and displays a single Cp* resonance at δ 1.09 ppm (lw = 15 Hz, 30 H) together with resonances at δ 21.7 (lw = 31 Hz, 2 H), 15.6 (lw = 16 Hz, 6 H), and 1.03 ppm (lw = 8 Hz, 3 H).

The diamagnetic lanthanum analogue of 5, $Cp^*_2LaOCMe_2CH_2C({=}O)Me$ (6), was prepared by a similar procedure. In its ^1H NMR spectrum, the CH_2 protons of the aldolate ring are present as a broad singlet at δ 2.24 ppm, which is in the chemical shift range reported for various metal aldolates.[8] The resonances of the aldolate methyl protons are, like the methylene protons, significantly broadened at room temperature (lw = 3–6 Hz), a strong indication of a dynamic process. Cooling down a toluene-d_8 sample of 6 to −80 °C resulted in a very complicated ^1H NMR spectrum with at least two Cp*-con-

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(6) Kinetic studies on lanthanide-catalyzed olefine hydrogenation are in accordance with this proposal. See: Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.

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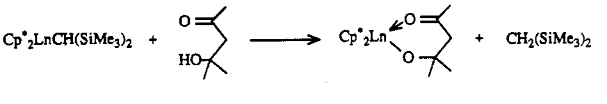
(8) (a) For a thorium aldolate, see: Sternal, R. S.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7920. (b) For aluminum aldolates, see: Power, M. B.; Apblett, A. W.; Bott, S. G.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 2529.

taining compounds present. This dynamic behavior is not as yet understood.[9] Furthermore, 6 is thermally less stable than the cerium analogue. The compound decomposes slowly in solution ($t_{1/2}$ ca. 2–3 days at 50 °C)[10] to yield a complex mixture with, among others, Cp*H present (NMR).

The aldolates **5** and **6** are also accessible by the reactions of the carbyls 1 and 2 with 1 mmol of 4-hydroxy-4-methyl-2-pentanone (NMR tube reactions; eq 4). The



5, Ln= Ce;
6, Ln= La

(4)

alcoholysis is best carried out at low temperatures (ca. −80 °C) to prevent Cp*H abstraction from the starting carbyls.[11] A preparative reaction using the cerium carbyl 2 afforded aldolate 5 in 74% yield. The spectroscopic features of this material are identical to that obtained from the reaction of 2 with acetone.

The C–C coupling of two molecules of acetone in an aldol fashion on a monomeric lanthanide center has not been reported in the literature, and to our knowledge, 5 is the first structurally characterized example of a lanthanide–aldolate.[12] The reactivity found for these early lanthanides is in marked contrast to the ketone chemistry reported for early transition metal and actinide alkyls and hydrides.[13] For the latter compounds, the carbonyl moiety always inserts into the M–C or M–H σ bond to form metal alkoxides, even with enolizable ketones such as acetone. The ketone chemistry of the early-lanthanide carbyls 1 and 2 resembles that of main-group organometallics such as organolithium and organoaluminum compounds.[14] Aldolates of these elements have recently been isolated and structurally characterized.[14c,15]

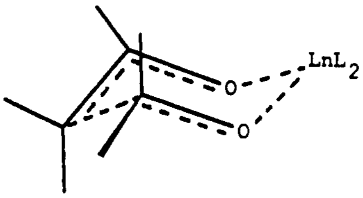


Figure 1. Proposed transition state for reactions of metal enolates with carbonyl compounds.

Table II. Selected NMR Data (δ) for Metal Enolates

	O—C_1(R)=C_2(H)R′		
compd	^{1}H NMR	^{13}C NMR	ref
[LiOC(*t*-Bu)=CH_2]$_n$	3.99 3.86	178 (C1), 78 (C2)	21
Cp_3ThOC(Me)=CH_2	4.09 3.95	165.4 (C1), 86.9 (C2)	22
[Cp_2Y(μ-OCH=CH_2)]$_2$	4.16 4.03	not reported	23
[Cp_2Lu(μ-OCH=CH_2)]$_2$	3.95 3.86	not reported	23
Cp*$_2$LaOCEt=C(H)-Me·O=CEt$_2$	4.26	161.5 (C1), 88.2 (C2)	this work

Hydrogen-transfer reactions in which 1 and 2 act as Brønstedt bases are not restricted to ketones only and appear to be the dominant reaction pathway for these early-lanthanide carbyls. For instance, we have already shown that acetonitrile is selectively metalated by 1 and 2 to give (cyanomethyl)lanthanides [Cp*$_2$LnCH$_2$CN]$_2$[16] whereas 2-alkynyllanthanides Cp*$_2$LnCH$_2$CCR (R = Me, Et, *n*-Pr) are formed upon reaction with disubstituted alkynes MeCCR.[17] These parallels in reactivity between main-group and early-lanthanide carbyls indicate that the Ln–C σ bond in 1 and 2 is rather polar.

A plausible mechanism for these early-lanthanide-centered aldol condensations is given in Scheme I and consists of two major steps. The first is the formation of a lanthanide enolate [Cp*$_2$LnOCR=CHR′]$_n$. Several pathways are conceivable for this step, e.g. acetone C–H bond activation followed by a 1,3-metal shift, protolysis of acetone in the enol form, or a concerted mechanism via a six-membered transition state. Coordination of a second molecule of acetone to the metal center followed by C–C coupling with the enolate fragment affords the aldol product. Stereochemical experiments for main-group alkyls and amides have indicated that C–C bond formation probably involves a cyclic transition state, organized by chelation to the metal center (Figure 1).[18] This model has successfully been applied to explain the stereochemical outcome of reactions of preformed zirconium[19] and boron enolates[20] with ketones and aldehydes.

An alternative mechanism, proposed by Marks et al.[8a] to explain the formation of a thorium aldolate from Cp*$_2$Th(Cl)–RuCp(CO)$_2$ and excess acetone, involves C–H

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(9) Elemental analysis for 6 is low in lanthanum and suggests the presence of some residual organic material, presumably acetone. A possible explanation for the observed dynamic behavior of 6 in solution is an exchange process between 6 and free acetone, either via dissociation of the aldolate carbonyl group or, more likely, via a labile, formally 9-coordinated 6–acetone adduct. The decreased thermal stability of 6 compared to 5 might also be caused by the presence of residual acetone. Further proof of this was obtained by treating the aldolates 5 and 6 with 1 mmol of acetone at room temperature. A slow reaction was observed in which all of the acetone was consumed and substantial amounts of Cp*H were formed, together with several unidentified organolanthanides.

(10) Under identical conditions, the $t_{1/2}$ value for the cerium aldolate 5 is about 8 days.

(11) Heeres, H. J.; Teuben,; J. H. Rogers, R. D. *J. Organomet. Chem.* **1989**, *364*, 87.

(12) Recently, Marks and co-workers have shown that the reaction of a heterobimetallic thorium–ruthenium compound, Cp*$_2$Th(Cl)–RuCp(CO)$_2$, with an excess of acetone yields a thorium aldolate, Cp*$_2$Th(Cl)-OCMe$_2$CH$_2$C(=O)Me together with CpRu(CO)$_2$H. See ref 8a.

(13) (a) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M. Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (c) Yasuda, H.; Tatsumi, K.; Nakamura, A. Acc. *Chem. Res.* **1985**, *18*, 120. (d) Ausema, J. B.; Hessen, B.; Teuben J. H. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 465. (e) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer-Verlag: Berlin, 1986.

(14) (a) Carey, F. A.; Sunberg, R. J. In *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1983; Part B, Chapter 10. (b) Heathcock, C. H. In *Comphrehensive Carbanion Chemistry*; Durst, T., Buncel, E., Eds.; Elsevier: Amsterdam, 1983; Part B, Vol. II. (c) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624.

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(21) Arnett, E. M.; Fisher, F. J.; Nichols, M. A.; Ribeiro, A. A. *J. Am. Chem. Soc.* **1990**, *112*, 801.

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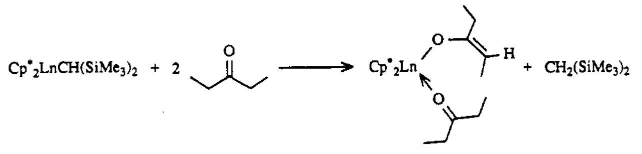
(23) Evans, W. J.; Dominquez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291.

bond activation of acetone to produce a metal–carbon σ bond followed by insertion of the C=O moiety of a second acetone molecule into this newly formed thorium–carbon bond.

Experiments with 3-pentanone indicate that a mechanism involving an enolate intermediate is the most likely for these lanthanide-centered reactions. Addition of 2 mmol of 3-pentanone to pentane solutions of the carbyls 1 and 2 resulted in the quantitative formation of $CH_2(SiMe_3)_2$ and a single organolanthanide product in >90% yield (NMR) for both lanthanum and cerium. Spectroscopic data suggest that these compounds are not the C–C-coupled aldol products but enolates with an additional molecule of 3-pentanone coordinated to the metal center (eq 5).



7, Ln= La;
8, Ln= Ce

(5)

The paramagnetic cerium derivative shows a single Cp* resonance at δ 2.8 ppm, four singlets for the enolate moiety with the correct integrated intensity (3:3:2:1), and two broad, upfield-shifted resonances for the coordinated 3-pentanone molecule. ^1H and ^{13}C NMR spectra of the diamagnetic lanthanum analogue are more informative and allow a comparison with the chemical shifts of known enolate species. The vinylic hydrogen is present as a quartet at the expected position (δ 4.26 ppm). The olefinic carbons are observed at δ 88.2 ppm (d, $^1J_{CH}$ = 150 Hz) and at δ 161.5 ppm. These chemical shifts are close to those reported for other metal enolate species (Table II). Furthermore, a clear downfield-shifted carbonyl resonance of the coordinated ketone is present at δ 226.8 ppm.[24] The geometry of the enolate moiety was determined by ^1H NMR NOE experiments on diamagnetic 7. A clear NOE effect was observed between the vinylic hydrogen of the enolate unit and the CH_2 protons of the ethyl group, indicating that these are oriented in a cis fashion.[25]

Further evidence that 7 and 8 are indeed enolates and not the C–C-coupled aldolate compounds was obtained by reacting paramagnetic 8 with another 1 equiv of 3-pentanone. Instead of separate resonances for free and coordinated 3-pentanone, significantly broadened and low-field-shifted resonances were observed for the methyl and methylene protons at δ −3.1 and −5.5 ppm, respectively. Hence, it appears that free and coordinated 3-pentanone are rapidly interconverting on the NMR time scale (eq 6). Such a dynamic process is not expected for metal aldolates and supports the proposal that 7 and 8 are true enolate species.[26]

(6)

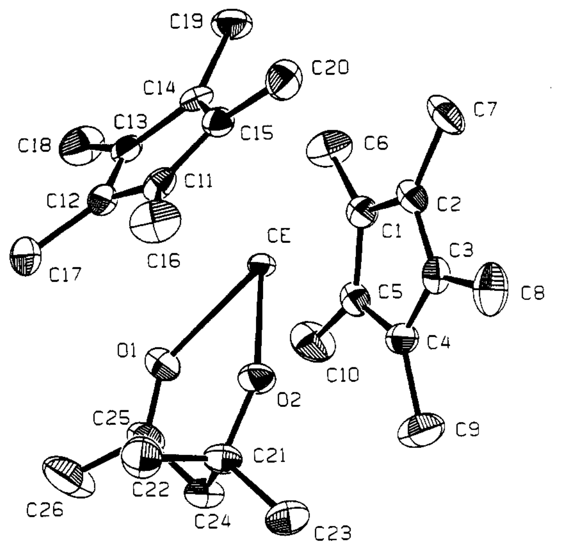


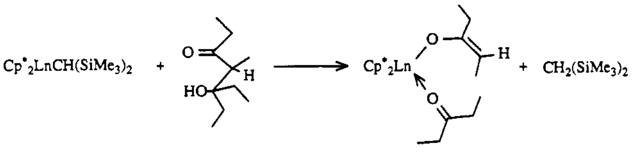
Figure 2. Perspective ORTEP view (50% level) of the cerium aldol compound 5. Hydrogen atoms have been omitted for clarity.

Table III. Selected Bond Distances and Angles for $Cp^*_2CeOCMe_2CH_2C(=O)Me$ (5)

	Bond Distances (Å)		
Ce–O(1)	2.506 (4)	C(21)–C(23)	1.54 (1)
Ce–O(2)	2.182 (4)	C(21)–C(24)	1.55 (1)
O(1)–C(25)	1.229 (7)	C(24)–C(25)	1.52 (1)
O(2)–C(21)	1.393 (7)	C(25)–C(26)	1.49 (1)
C(21)–C(22)	1.52 (1)		
	Bond Angles (deg)		
O(1)–Ce–O(2)	73.7 (1)	O(1)–C(25)–C(24)	121.3 (6)
Ce–O(1)–C(25)	131.1 (4)	Ce–O(2)–C(21)	144.0 (4)
C(24)–C(21)–O(2)	109.9 (5)	Cent-Ce-Cent[a]	133.6

[a] Cent = center of gravity of a Cp* ring.

Attempts to induce C–C coupling and to prepare the aldol compounds of 3-pentanone by heating a solution of the lanthanum enolate 7 were not successful. After 3 days at 50 °C, significant amounts of Cp*H had been formed together with at least three unidentified organolanthanum species. Due to the complexity it was not possible to determine whether C–C coupling had taken place. However, the reactions of the carbyls 1 and 2 with 4-methyl-5-hydroxy-5-ethyl-3-heptanone clearly indicate that the enolate–3-pentanone adducts 7 and 8 are thermodynamically favored. Instead of formation of the aldolates, as found for 4-hydroxy-4-methyl-2-pentanone, C–C bond cleavage occurred and 7 and 8 were formed in essentially quantitative yields (NMR; eq 7). Hence, it appears that the differences in reactivity between acetone and 3-pentanone in these early-lanthanide-promoted reactions are thermodynamic in origin.



7, Ln= La;
8, Ln= Ce

(7)

We are currently investigating the ketone chemistry of Cp^*_2LnR carbyls with smaller carbyl groups (allyl, benzyl,

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[24] The carbonyl resonance of free 3-pentanone is present at δ 210.7 ppm. See: Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C-NMR Spektroskopie*; Thieme-Verlag: Stuttgart, New York, 1984.

[25] ^1H NMR NOE experiments on the cerium derivative 8 suggest a similar cis arrangement.

[26] Several attempts have been made to determine the molecular structures of 7 and 8 with single-crystal X-ray diffraction. Unfortunately, proper data sets could not be obtained so far.

methyl) to determine whether the observed reactivity, i.e. enolate or aldolate formation, is a general reaction pathway for early-lanthanide carbyls or is just restricted to compounds with very bulky alkyl groups.

Molecular Structure of $Cp^*_2CeOCMe_2CH_2C(=O)Me$ (5). The molecular structure of **5** was determined by single-crystal X-ray diffraction, and the result is depicted in Figure 2. Key distances and angles are given in Table III; final fractional coordinates are given in Table IV. The compound crystallizes in monomeric units with the central cerium atom in a distorted tetrahedral environment.

The centroid–Ce–centroid angle is 133.6°, which is in the range for various $Cp^*_2Ln^{III}$ compounds.[27] The average cerium–carbon ring distances are 2.81 (1) Å for ring 1 (C(1)–C(5)) and 2.83 (1) Å for ring 2 (C(11)–C(15)). Of particular interest is the bonding of the chelating aldol ligand. As expected, the cerium–oxygen distances differ significantly. The Ce-O(2) distance is 2.182 (4) Å, which is in the range for Ce–O distances in cerium compounds with aryloxide ligation (2.14–2.28 Å).[28] The cerium carbonyl–oxygen bond distance (Ce–O(1)) is much longer: 2.506 (4) Å. Noteworthy is the disparity between the traditional boat or chair conformation of a six-membered ring and the conformation of the aldol ligand. Ce(1)-O(1)-C(25)-C(21)-O(2) are coplanar within 0.07 Å with C(24) 0.69 Å out of this plane. The structural features of the six-membered ring resemble those of the lithiated aldol compound derived from pivaldehyde and the lithium enolate of pinacolone, one of the few structurally characterized lithiated aldol products.[15] The relation between the conformation of the six-membered ring and the actual transition state for the aldol reaction, however, remains speculative.

Conclusions

The reactivity of the early-lanthanide carbyls $Cp^*_2LnCH(SiMe_3)_2$ (Ln = La, Ce) with ketones is dominated by hydrogen-transfer reactions (C–H bond activation/deprotonation) producing lanthanide enolates or aldolates. Enolate/aldolate formation is substrate dependent, and clear differences were observed between acetone and 3-pentanone. Experiments with the corresponding β-hydroxy ketones suggest that these differences are thermodynamic and not kinetic in origin. The ketone chemistry of these early-lanthanide carbyls resemble that of the main-group elements Li, Na, B, and Al. Detailed mechanistic studies on the latter elements are often seriously hampered due to the formation of highly fluctional enolate and aldolate aggregates in solution.[14c,21] Although further detailed mechanistic and structural studies will be required, it seems that organolanthanides supported by two pentamethylcyclopentadienyl ligands may serve as *monomeric* models for aldol condensations and thus provide valuable insights into the mechanism of this important C–C bond-forming reaction.

Experimental Section

General Considerations. All organolanthanide compounds described here are extremely air-sensitive, and manipulations were carried out by using Schlenk, vacuum-line, or glovebox techniques under nitrogen or argon. Benzene, toluene, diethyl ether, THF, and pentane were distilled from Na/K alloy and stored under an inert atmosphere. NMR solvents were distilled from Na or Na/K alloy. The lanthanide carbyls $Cp^*_2LnCH(SiMe_3)_2$ (**1**, Ln = La; **2**, Ln = Ce) were prepared from $[Cp^*_2LnCl]_n$ and $LiCH(SiMe_3)_2$ according to a published procedure.[5a] $[Cp^*_2LaH]_2$ (**3**) was synthesized by hydrogenolysis of carbyl **1** according to ref 5b. Acetone, 3-pentanone, 4-hydroxy-4-methyl-2-pentanone, 4-methyl-5-hydroxy-5-ethyl-3-heptanone,[29] and di-*tert*-butyl ke-

Table IV. Positional Parameters and *B*(eq) Values for 5

atom	*x*	*y*	*z*	*B*(eq), Å²
Ce	0.02091 (3)	0.24272 (1)	0.83361 (2)	1.60 (1)
O(1)	0.2046 (4)	0.1484 (2)	0.8725 (3)	2.7 (2)
O(2)	-0.0232 (4)	0.1465 (2)	0.7366 (3)	2.6 (2)
C(1)	-0.0322 (5)	0.2754 (3)	1.0144 (4)	2.0 (2)
C(2)	-0.1481 (6)	0.2948 (3)	0.9534 (4)	2.1 (2)
C(3)	-0.2045 (5)	0.2251 (3)	0.9143 (4)	2.2 (2)
C(4)	-0.1244 (6)	0.1634 (3)	0.9528 (4)	2.3 (2)
C(5)	-0.0169 (6)	0.1947 (3)	1.0134 (4)	2.1 (2)
C(6)	0.0538 (8)	0.3294 (4)	1.0785 (5)	3.0 (3)
C(7)	-0.2143 (8)	0.3721 (4)	0.9392 (6)	3.4 (3)
C(8)	-0.3294 (7)	0.2175 (6)	0.8477 (6)	3.9 (4)
C(9)	-0.157 (1)	0.0796 (4)	0.9400 (6)	3.8 (4)
C(10)	0.0890 (9)	0.1504 (5)	1.0747 (6)	3.5 (3)
C(11)	0.0882 (6)	0.3314 (3)	0.6863 (4)	2.2 (2)
C(12)	0.2102 (5)	0.3124 (3)	0.7405 (4)	2.1 (2)
C(13)	0.2209 (5)	0.3521 (3)	0.8263 (4)	2.1 (2)
C(14)	0.1074 (5)	0.3982 (3)	0.8242 (4)	1.9 (2)
C(15)	0.0239 (6)	0.3844 (3)	0.7382 (4)	2.1 (2)
C(16)	0.038 (1)	0.3053 (5)	0.5876 (5)	3.8 (3)
C(17)	0.3163 (7)	0.2631 (4)	0.7114 (6)	3.4 (3)
C(18)	0.3365 (8)	0.3488 (5)	0.9035 (6)	3.4 (3)
C(19)	0.0892 (8)	0.4603 (4)	0.8933 (5)	3.0 (3)
C(20)	-0.1025 (7)	0.4253 (4)	0.7035 (6)	3.2 (3)
C(21)	0.0202 (6)	0.0746 (3)	0.7115 (5)	2.8 (3)
C(22)	0.0998 (8)	0.0833 (5)	0.6332 (6)	4.0 (4)
C(23)	-0.0982 (9)	0.0228 (5)	0.6779 (7)	4.4 (4)
C(24)	0.1024 (7)	0.0354 (4)	0.7976 (6)	3.6 (3)
C(25)	0.2184 (6)	0.0824 (3)	0.8447 (4)	2.7 (3)
C(26)	0.350 (1)	0.0462 (6)	0.8594 (8)	5.0 (5)
H(6A)	0.154 (7)	0.317 (4)	1.073 (5)	4 (2)
H(6C)	0.029 (7)	0.383 (5)	1.064 (5)	6 (2)
H(6B)	0.047 (7)	0.321 (4)	1.145 (5)	4 (2)
H(7B)	-0.157 (6)	0.414 (4)	0.978 (5)	4 (2)
H(7C)	-0.299 (7)	0.367 (4)	0.956 (5)	5 (2)
H(7A)	-0.210 (7)	0.392 (4)	0.881 (5)	4 (2)
H(8B)	-0.352 (7)	0.268 (4)	0.827 (5)	5 (2)
H(8A)	-0.397 (8)	0.215 (4)	0.880 (5)	5 (2)
H(8C)	-0.326 (7)	0.173 (5)	0.808 (6)	6 (2)
H(9B)	-0.10 (1)	0.045 (6)	0.974 (8)	11 (4)
H(9A)	-0.190 (7)	0.070 (4)	0.879 (5)	4 (2)
H(9C)	-0.23 (1)	0.064 (5)	0.966 (7)	8 (3)
H(10A)	0.097 (6)	0.101 (4)	1.043 (4)	3 (1)
H(10C)	0.15 (1)	0.178 (7)	1.086 (8)	11 (4)
H(10B)	0.08 (1)	0.142 (6)	1.143 (7)	9 (3)
H(16C)	-0.03 (1)	0.270 (6)	0.587 (7)	9 (3)
H(16A)	0.101 (9)	0.277 (5)	0.566 (6)	7 (2)
H(16B)	0.02 (1)	0.343 (7)	0.54 (1)	14 (4)
H(17C)	0.355 (7)	0.223 (4)	0.766 (5)	5 (2)
H(17B)	0.391 (7)	0.290 (4)	0.712 (5)	4 (2)
H(17A)	0.289 (6)	0.247 (3)	0.653 (5)	3 (2)
H(18A)	0.415 (9)	0.367 (5)	0.896 (6)	6 (2)
H(18B)	0.316 (8)	0.369 (5)	0.960 (6)	6 (2)
H(18C)	0.377 (9)	0.306 (5)	0.907 (6)	6 (2)
H(19A)	0.140 (7)	0.449 (4)	0.961 (5)	4 (2)
H(19C)	0.013 (8)	0.461 (4)	0.906 (5)	5 (2)
H(19B)	0.104 (6)	0.516 (3)	0.868 (4)	3 (1)
H(20C)	-0.103 (8)	0.479 (5)	0.727 (6)	7 (2)
H(20A)	-0.178 (6)	0.407 (3)	0.716 (4)	2 (1)
H(20B)	-0.116 (7)	0.430 (4)	0.633 (5)	4 (2)
H(22A)	0.179 (6)	0.113 (3)	0.656 (4)	3 (1)
H(22B)	0.134 (7)	0.029 (4)	0.623 (5)	5 (2)
H(22C)	0.028 (7)	0.101 (4)	0.577 (5)	5 (2)
H(23A)	-0.151 (8)	0.012 (4)	0.733 (6)	6 (2)
H(23C)	-0.072 (9)	-0.023 (5)	0.669 (6)	7 (3)
H(23B)	-0.156 (8)	0.045 (5)	0.619 (6)	6 (2)
H(24B)	0.147 (7)	-0.019 (4)	0.799 (5)	6 (2)
H(24A)	0.056 (6)	0.023 (3)	0.852 (4)	3 (1)
H(26A)	0.34 (1)	0.005 (5)	0.889 (6)	7 (3)
H(26B)	0.420 (8)	0.089 (5)	0.879 (6)	6 (2)
H(26C)	0.37 (1)	0.040 (5)	0.799 (7)	8 (3)

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tone were distilled or vacuum transferred prior to use and stored over molecular sieves in an inert atmosphere. IR spectra were recorded on a Pye-Unicam SP3-300 or a Mattson-4020 Galaxy FT-IR spectrophotometer using Nujol mulls between KBr disks. NMR spectra were recorded on a Brucker WH-90 or a Varian VXR-300 spectrometer. Chemical shifts are reported in parts per million relative to TMS (δ 0.00 ppm). Proton spectra are referenced to residual protons in deuterated solvents (benzene-d_6, δ 7.15; toluene-d_8, δ 7.02 ppm) or TMS. ^{13}C NMR resonances are referenced to carbon resonances of the deuterated solvent (benzene-d_6, δ 127.96; toluene-d_8, δ 20.4 ppm). Elemental analysis were performed at the Microanalytical Department of the Chemistry Department of the University of Groningen. All percentages found are the average of at least two independent determinations.

NMR Tube Reactions of $Cp*_2LnCH(SiMe_3)_2$ (1, Ln = La; 2, Ln = Ce) with Excess of Di-*tert*-butyl Ketone. 1. A 23-μL (0.13-mmol) amount of di-*tert*-butyl ketone was added to an NMR tube charged with 37.5 mg (0.067 mmol) of 1 in benzene-d_6 (0.5 mL). The tube was sealed and stored at 50 °C. After 4 days at room temperature, the starting materials were still present.

2. The reaction with the cerium carbyl 2 was performed analogously with 27.9 mg (0.049 mmol) of 2 and 15 μL (0.099 mmol) of di-*tert*-butyl ketone.

Preparation of $Cp*_2LaOCH(t\text{-}Bu)_2{\cdot}O{=}C(t\text{-}Bu)_2$ (4). A 256-μL (1.48-mmol) amount of di-*tert*-butyl ketone was added to a suspension of $[Cp*_2LaH]_2$ (292 mg, 0.35 mmol) in pentane (20 mL). All of the hydride dissolved within 10 min, and a clear yellow solution was formed. After being stirred for 15 min at room temperature, the solution was concentrated and cooled to −80 °C. Isolation gave 313 mg (0.45 mmol, 64%) of 4 as well-formed yellow needles. IR (cm^{-1}): 2725 (w), 1690 (w), 1630 (s), 1540 (w), 1230 (w), 1160 (w), 1060 (s), 1035 (m), 1000 (s), 980 (m), 950 (w), 770 (w), 630 (m), 590 (w), 550 (w). NMR data are given in Table I. Anal. Calcd for $C_{38}H_{67}LaO_2$: C, 65.68; H, 9.72; La, 19.99. Found: C, 65.85; H, 9.84; La, 19.63.

Preparation of $Cp*_2CeOCMe_2CH_2C({=}O)Me$ (5). A 332-mg (0.58-mmol) amount of 2 was dissolved in 20 mL of pentane. The solution was cooled to −70 °C, and 86 μL (1.17 mmol) of acetone was added. The solution was allowed to warm to room temperature, concentrated, and subsequently cooled to −80 °C, during which deep red crystals of 5 deposited. Yield: 137 mg (0.26 mmol, 46%). IR (cm^{-1}): 2710 (w), 2140 (m), 1680 (m), 1660 (s), 1410 (m), 1360 (s), 1320 (m), 1250 (m), 1210 (m), 1170 (sh), 1160 (s), 1010 (s), 950 (m), 770 (m), 640 (m), 560 (m), 510 (m), 460 (m). NMR data are given in Table I. Anal. Calcd for $C_{26}H_{41}CeO_2$: C, 59.40; H, 7.86; Ce, 26.65. Found: C, 59.44; H, 7.73; Ce, 26.54.

The lanthanum analogue (6) was prepared by a similar procedure using 320 mg (0.56 mmol) of 1 and 83 μL (1.13 mmol) of acetone. Workup gave 196 mg (0.37 mmol, 66%) of 6 as yellow crystals. IR (cm^{-1}): 2720 (w), 1680 (s), 1660 (s), 1640 (s), 1350 (m), 1300 (w), 1250 (m), 1150 (s), 1080 (m), 990 (s), 930 (m), 880 (m), 720 (m), 600 (m), 540 (m), 480 (m). NMR data are given in Table I. Anal. Calcd for $C_{26}H_{41}LaO_2$: C, 59.54; H, 7.88; La, 26.48. Found: C, 59.36; H, 7.92; La, 25.72.

Reactions of 1 and 2 with 4-Hydroxy-4-methyl-2-pentanone. (a) Preparative Reaction for Ce. A 78-μL (0.63-mmol) amount of 4-hydroxy-4-methyl-2-pentanone was added to a cooled pentane solution (−80 °C, 10 mL) of 2 (354 mg, 0.62 mmol). The solution was allowed to warm to room temperature and subsequently concentrated to ca. 5 mL. Upon cooling of the solution to −80 °C, red needles of 5 settled. Yield: 244 mg (0.46 mmol, 74%). IR and NMR are identical to that of the crystals obtained from the reaction of 2 with 2 equiv of acetone.

(b) NMR Tube Reaction for Ce. A 6.9-μL (0.055-mmol) amount of 4-hydroxy-4-methyl-2-pentanone was added to a cooled solution (−80 °C) of 2 (31.4 mg, 0.055 mmol) in toluene-d_8 (0.5 mL). The tube was sealed, and the reaction was monitored with NMR spectroscopy. After ca. 30 min at room temperature characteristic resonances of 2 had disappeared and 5 together with $CH_2(SiMe_3)_2$ had formed in essential quantitative yields.

(c) NMR Tube Reaction for La. The reaction was carried out as described for cerium with 6.3 μL (0.05 mmol) of 4-hydroxy-4-methyl-2-pentanone and 28.6 mg (0.05 mmol) of 1.

Table V. Crystal Structure Analysis and Crystal Data for $Cp*_2CeOCMe_2CH_2C({=}O)Me$

compd	$C_{26}H_{41}CeO_2$
mol wt	525.7
space group	$P2_1/n$
a, Å	10.386 (5)
b, Å	17.32 (1)
c, Å	14.488 (3)
β, deg	99.33 (3)
V, Å^3	2572 (2)
Z	4
D_{calcd}, g·cm^{-3}	1.36
μ(Mo Kα), mm^{-1}	1.81
max cryst dimens, mm	0.40 × 0.40 × 0.40
scan width, deg	1.21 + 0.30 tan θ
no. of reflcns measd	4677
2θ range, deg	3.5–50
no. of obsd reflctns	3343 ($I > 3\sigma(I)$)
no. of params varied	426
R	0.035
R_w	0.041

Preparation of $Cp*_2CeOC(Et){=}C(H)Me{\cdot}O{=}CEt_2$ (8). A 417-mg (0.73-mmol) amount of 2 was dissolved in pentane (20 mL). The solution was cooled to −80 °C, and 153 μL (1.44 mmol) of 3-pentanone was added. The solution was allowed to warm to room temperature and stirred for another 1 h. Concentration and cooling to −80 °C gave 123 mg (0.21 mmol) of 8 as red crystals. A second low-temperature crystallization afforded another 95 mg (0.16 mmol). Total yield: 0.37 mmol, 51%. IR (cm^{-1}): 2730 (w), 2140 (w), 1670 (s), 1640 (s), 1340 (s), 1190 (s), 1100 (m), 1060 (m), 1040 (s), 1030 (s), 960 (m), 830 (m), 740 (m), 510 (m). NMR data are given in Table I. Anal. Calcd for $C_{30}H_{49}CeO_2$: C, 61.93; H, 8.49; Ce, 24.08. Found: C, 61.75; H, 8.44; Ce, 24.09.

The lanthanum derivative 7 was prepared by a similar procedure using 257 mg (0.45 mmol) of 1 and 78 μL (0.77 mmol) of 3-pentanone. Workup gave 142 mg (0.24 mmol, 53%) of 7 as yellow needles. IR (cm^{-1}): 2710 (w), 1720 (w), 1670 (s), 1640 (m), 1340 (m), 1190 (m), 1080 (m), 1060 (m), 1030 (m), 950 (m), 850 (m), 720 (m). NMR data are given in Table I. Anal. Calcd for $C_{30}H_{49}LaO_2$: C, 62.06; H, 8.51; La, 23.92. Found: C, 61.77; H, 8.51; La, 24.16.

NMR Tube Reaction of 8 with 3-Pentanone. A 32-mg (0.056-mmol) amount of 8 was dissolved in benzene-d_6 (0.5 mL). A 6.0-μL (0.059-mmol) amount of 3-pentanone was added, and the tube was sealed. ^{1}H NMR spectroscopy shows two significantly broadened resonances for the methyl and methylene groups of 3-pentanone at δ −3.1 (lw = 96 Hz) and δ −5.5 (lw = 300 Hz), respectively, indicative of a dynamic process in which free and coordinated 3-pentanone are rapidly interconverted on the NMR time scale. The other resonances of 8 are not significantly affected.

Reactions of 1 and 2 with 4-Methyl-5-hydroxy-5-ethyl-3-heptanone. (a) Preparative Reaction for La. A 67-μL (0.36-mmol) amount of 4-methyl-5-hydroxy-5-ethyl-3-heptanone was added at −80 °C to a stirred solution of 1 (213.8 mg, 0.38 mmol) in pentane (15 mL). The solution was allowed to warm to room temperature. Concentrating and cooling gave 174 mg (0.30 mmol, 79%) of 7 as yellow crystals. IR and ^{1}H NMR data are identical to that of the crystals obtained by reacting 1 with 2 mmol of 3-pentanone.

(b) NMR Tube Reaction for La. A 9-μL (0.048-mmol) amount of 4-methyl-5-hydroxy-5-ethyl-3-heptanone was added to a cooled solution (−80 °C) of 1 (24.6 mg, 0.043 mmol) in toluene-d_8 (0.5 mL). The tube was sealed, and the reaction was monitored with NMR spectroscopy. After 30 min at room temperature, 7 was formed essentially quantitative.

(c) NMR Tube Reaction for Ce. The reaction was carried out as described for lanthanum with 36.5 mg (0.064 mmol) of 2 and 13 μL (0.069 mmol) of 4-methyl-5-hydroxy-5-ethyl-3-heptanone.

Crystal Data, Structure Determination, and Refinement for $Cp*_2CeOCMe_2CH_2C({=}O)Me$ (5). A red crystal of the title compound, obtained by cooling a pentane solution to −30 °C, was mounted in epoxy resin on a glass fiber and transferred to a Rigaku AFC6R diffractometer. Diffracted intensities were measured at

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-150 ± 1 °C using graphite-monochromated Mo Kα radiation from a RU200 rotating anode operated at 9 kW (50 kV; 180 mA). The $\omega/2\theta$ scan mode was employed with an ω scan rate of 32° min^{-1}. Weak reflections ($F < 10\sigma(F)$) were rescanned up to three times and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time vs background time was 2:1. Of the 4677 independent reflections measured, 3343 had $I > 3\sigma(I)$ and were regarded as being observed. That the crystal was not subject to decay during the measurement of intensities was checked by monitoring three reflections at regular intervals (150 reflections). Intensity data were corrected for Lorentz and polarization effects but not for absorption. Unit cell parameters were obtained from diffractometer setting angles for 25 reflections in the range $47° < 2\theta < 49°$. The structure was solved by direct methods (MITHRIL)[30] and subsequent electron density calculations. Full-matrix least-squares refinement of positional anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms, located from a difference map, gave a final $R = 0.035$ and $R_w = 0.041$ for 426 parameters and 3343 reflections. Atomic scattering factors and anomalous dispersion corrections were taken from ref 31, and the F_o values were weighted according to $w = [\sigma^2(F_o)]^{-1}$. A final difference map showed a maximum and minimum residual electron densities of 1.25 and -0.82 e·Å^{-3}, respectively. All calculations were carried out with the TEXSAN program system.[32] Crystal data and experimental details of the structure determination are compiled in Table V.

Acknowledgment. Financial support from Shell Research B.V. is gratefully acknowledged.

Registry No. 1, 98720-36-6; 2, 106333-13-5; 4, 137232-35-0; 5, 137232-36-1; 6, 137232-37-2; 7, 137232-38-3; 8, 137232-39-4; [Cp*$_2$LaH]$_2$, 98720-39-9; (Me$_3$Si)$_2$CH$_2$, 2117-28-4; di-*tert*-butyl ketone, 815-24-7; acetone, 67-64-1; 4-hydroxy-4-methyl-2-pentanone, 123-42-2; 3-pentanone, 96-22-0; 4-methyl-5-hydroxy-5-ethyl-3-heptanone, 3677-86-9.

Supplementary Material Available: For 5, tables of bond distances and angles, torsion angles, and thermal parameters (17 pages); a full listing of F_o, F_c, and $\sigma(F)$ values (31 pages). Ordering information is given on any current masthead page.

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Reactions of (OC)$_{3,2}$Fe$^{\bullet-}$ and (OC)$_{4,3}$Mn$^-$ with Trimethylsilane, Silane, and Germane

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Received July 9, 1991

(OC)$_3$Fe$^{\bullet-}$ and (OC)$_4$Mn$^-$ reacted with Me$_3$SiH, SiH$_4$, and GeH$_4$ to yield the corresponding adducts. The smaller rate constants for the (OC)$_4$Mn$^-$ reactions are attributed to different spin multiplicities of the starting and product ions. (OC)$_2$Fe$^{\bullet-}$ and (OC)$_3$Mn$^-$ reacted rapidly with Me$_3$SiH to give the products of dehydrogenation, (OC)$_x$M(η^2-CH$_2$=Si(CH$_3$)$_2$)$^-$, which added additional Me$_3$SiH to form the corresponding adducts; the latter reaction also formed the adduct negative ions as primary products. (OC)$_2$Fe$^{\bullet-}$ (mainly) and (OC)$_3$Mn$^-$ (exclusively) reacted rapidly with silane to yield the product ions of α-dehydrogenation, (OC)$_x$M(H)(≡SiH)$^-$. The reaction of (OC)$_3$Mn(D)$_2^-$ with silane formed mainly the (adduct − H$_2$ − D$_2$)$^-$, (adduct − HD)$^-$, and (adduct − D$_2$)$^-$ products. With germane as the neutral reactant, (OC)$_2$Fe$^{\bullet-}$ and (OC)$_3$Mn$^-$ reacted rapidly to give the germylide complexes (OC)$_x$M(=Ge)$^-$ as the major or exclusive product, respectively. The germylide complex negative ions reacted with excess germane to produce the corresponding adducts. Lower limits for the binding energies of the CH$_2$–Si(CH$_3$)$_2$ and Ge atom ligands to the metal centers of these negative ions are given.

The success in the oxidative insertion of the 13-electron transition-metal complex negative ion (OC)$_2$Fe$^{\bullet-}$ into the C–H bonds of methane and 2,2-dimethylpropane yielding the corresponding hydrido–alkyl complexes[1] stimulated our interest in the corresponding reactions with the other available group 14 hydrides silane and germane. Additions of Si–H[2] and Ge–H bonds[3] to multiple bonds in unsaturated hydrocarbons, aldehydes, and ketones are catalyzed by transition-metal complexes. Although hydrosilation and hydrogermylation reactions are often complex and the mechanisms are not well understood, oxidative insertion of the coordinatively unsaturated metal center into the Si–H or Ge–H bond is assumed to be required in the process.[4]

Kang, et al.[5] reported the gas-phase reactions of Ni$^+$, Co$^+$, Fe$^+$, Cr$^+$, V$^+$, and Ti$^+$ atomic cations with silane and various methylated silanes. With SiH$_4$, Ni$^+$, Co$^+$, and Ti$^+$ reacted to produce the corresponding (adduct − H$_2$)$^+$ ions assumed to have the M=SiH$_2^+$ structures.[6] The reactions with the methylsilanes, (CH$_3$)$_x$SiH$_{4-x}$ where x = 1–4, gen-

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(6) We use the formalism M=SiH$_2$ and M=Ge (Si and Ge as 2-electron donors), and M≡SiH and M≡GeH (Si and Ge as 3-electron donors) to be consistent with the valence of the Si and Ge atoms rather than designating the number of σ-bonds in the structure. In each case, π-back-bonding from the metal to Si or Ge is involved as one of the multiple bonds.

0276-7333/92/2311-0356$03.00/0